

Measuring VOCs for the study of atmospheric processes

AIR POLLUTION IS related to many complex atmospheric processes. Present research is focused on some of these processes such as acid deposition, ozone formation and depletion, oxidation reactions, and local pollution caused by emissions from mobile and stationary sources. To understand these processes in order to control them, it is important to gather information on all relevant compounds and their behavior under specific atmospheric conditions.

In general, two different approaches may be distinguished: monitoring and modeling. Neither monitoring nor modeling can be used by itself to describe the status of the atmosphere with relation to air pollution. The two are in fact complementary. Progress in the knowledge of atmospheric chemistry has resulted in a more and more detailed description of many atmospheric processes. Organic compounds play an important role in a number of these processes and monitoring these compounds is of utmost importance. Monitoring systems for organic compounds should comply as much as possible with the specifications of the systems used for monitoring inorganic compounds like carbon monoxide, nitrogen monoxide, nitrogen dioxide, and ozone. Monitors for these compounds allow nearly real-time concentration measurements, often using specific detection principles, and are designed for long, unattended operation.

Compared to inorganic compounds, volatile organic components are numerous and often very similar to each other, and therefore specific detection is extremely difficult. For this reason chromatography is the most suitable method. However, standard chromatographic equipment has two major complications if it is to be used for monitoring purposes: real-time monitoring is not possible since the separation processes can take considerable time, and furthermore, during the analysis the system is generally not available for sample introduction. These considerations and the specifications for a monitoring system have formed the basis for the design of a monitoring system for volatile organic compounds in air, described in this paper—the VOC air analyzer

(VOCAA) (Chrompack International, Middelburg, The Netherlands).

Design considerations

Generally, the time scale of atmospheric processes lies within the range of 30 min to 3 hr. It is normally also the time unit used in models. This characteristic implies that real-time monitoring may be restricted to the analysis of a time integrated sample collected over a period of 30 min to 3 hr. The information obtained will therefore sufficiently indicate the fluctuations of relevant compounds. The sample has to be representative for the entire period and hence collection must take place during the (major part of the) period. A second consideration is that none of the integrated samples may be omitted. This suggests that sample collection and sample analysis of the previous collected sample have to be performed simultaneously. This is easily sustained, except for the calibration sample to be analyzed. Note that if the moment for calibration is shifted through the day (i.e., calibration is performed once every 23 hr), the loss of information is not systematic.

The monitoring system should be installed in remote stations. Therefore, unattended operation for an extended period of time, perhaps three to four weeks, is required. Consequently, supplies must be available in sufficient quantities or have to be generated on site using only electrical energy. Energy should not be generated by a fuel consuming generator, since this will possibly emit compounds belonging to the target group.

A commonly used division of organic compounds is based on the boiling point. Two groups are considered relevant for this monitor system: VVOC (very volatile organic compounds) and VOC (volatile organic compounds). Compounds belonging to these groups can occur in the gaseous phase at ambient temperatures at sub- $\mu\text{g}/\text{m}^3$ levels or higher. Due to the large difference between the concentrations of methane and the other compounds of the groups in air, and due to the relative small temporal and spacial variation of methane, this compound is usually omitted.

In the recent past, cryogenic preconcentrators and capillary gas chromatographic techniques have been used for the analysis of these compounds.^{1,2} Special columns have been developed for the groups VVOC and VOC.³ These techniques and the above-mentioned considerations have resulted in the design of the VOCAA. The design and application will also be described.

Dr. Bloemen is Head of the Methods Development Section of the Laboratory of Air Research of the National Institute of Public Health and Environmental Protection, Mr. Bos is chromatographic analyst at the same institute. Dr. Dooper is product manager, Environmental Analyzers at Chrompack International, Middelburg, The Netherlands.

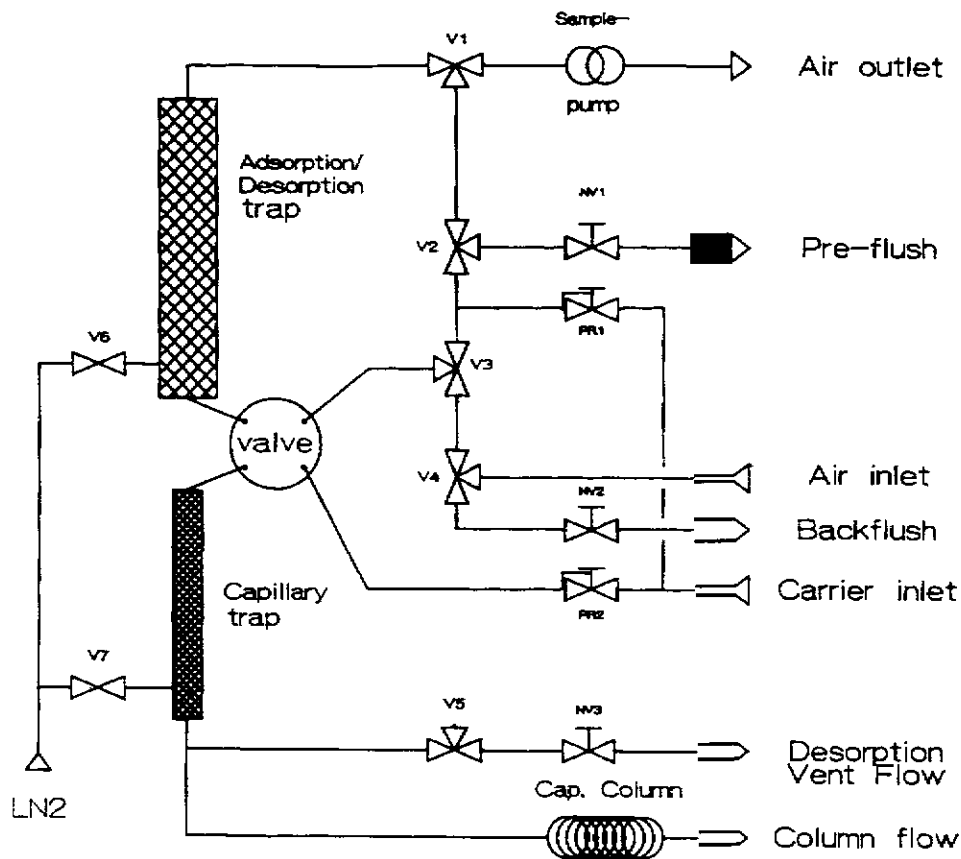


Figure 1 Schematics of the volatile organic compound air analyzer (VOCCA).

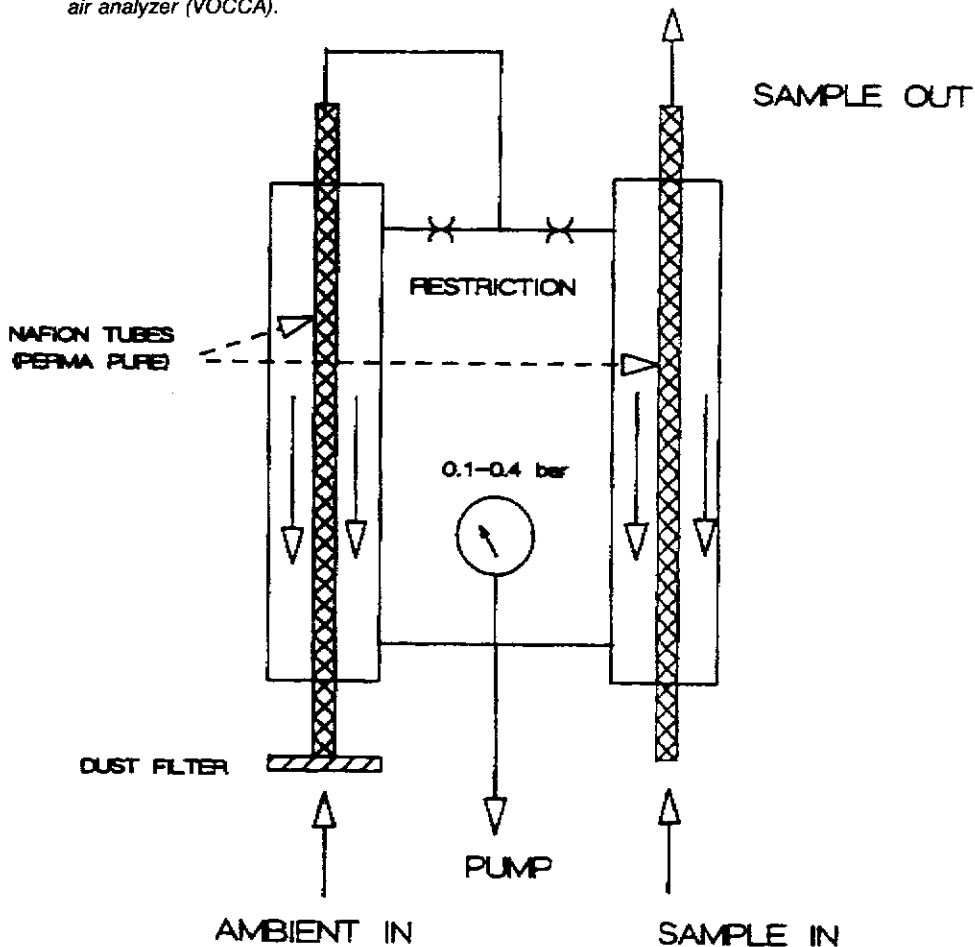


Figure 2 Self-regenerating sample stream dryer.

Design

The VOCAA comprises a sampler and injector, a gas chromatograph equipped with a flame ionization detector (FID), an electron capture detector (ECD), and an integrator and data processor. These constitute the monitoring system for VVOCs and VOCs.

The VOCAA (schematically presented in *Figure 1*) has been designed to simultaneously sample and analyze air using (cryo) adsorption and thermal desorption techniques. Control of the heating and cooling devices, valves, and sampling pump, as well as the synchronization with the gas chromatograph and the integrator-data processor, is performed by the VOCAA-controller.

In the sample collection mode, air is drawn through the valve and the adsorption trap by means of a sample pump with a flow ranging from 10 to 70 mL/min. The adsorption trap filled with appropriate trapping materials such as Tenax (Enka America, Inc., Asheville, North Carolina, U.S.A.), (Supelco, Inc., Bellefonte, Pennsylvania, U.S.A.), Carbosieve, or Carbotrap, or a composition of these materials, is cooled using liquid nitrogen to a temperature ranging from $-180\text{ }^{\circ}\text{C}$ to subambient. Recent developments in adsorbent manufacturing⁴ enable a detailed tuning of the adsorption characteristics of the trap. Moisture is selectively removed on-line by passing the sample stream through a two-stage dryer [Nafion[®] tubes, DuPont Corp. (Wilmington, Delaware), *Figure 2*] reducing the dew point to $-55\text{ }^{\circ}\text{C}$. This two-stage dryer is self-regenerating. The drying force is the moisture gradient generated by the underpressure (0.1 atm absolute) in the first stage. The dry air stream is used in the second stage to dry the sample stream. It is estimated that replacement of the drying system will be needed every six months to guarantee optimal performance.

Just before the end of a sampling period, the capillary trap is cooled to a temperature within the range of $-180\text{ }^{\circ}\text{C}$ to subambient (cooling rate $100\text{ }^{\circ}\text{C}/\text{min}$). The adsorption trap may be flushed with carrier gas, removing any nontrapped compounds, including oxygen, present in the last portion of the sample.

In the sample transfer mode, the trapped compounds are transferred from the adsorption trap to the capillary trap using a reversed carrier gas flow. The capillary trap consists of a wide bore fused silica capillary coated with liquid phase and/or filled with adsorbent. The transfer is induced by heating the adsorption trap (heating rate $190\text{ }^{\circ}\text{C}/\text{min}$) and switching of the valve. Only in this mode are the sampler and the injector connected. While in this mode, the temperature of the capillary trap is maintained at the low temperature set during the precool. To minimize discrimination of the higher boiling compounds and sample transfer time, the transfer flow is higher than the flow defined in the restriction of the capillary column. This is achieved by opening

the desorption vent. After the completion of the transfer, the valve is switched again.

While in the injection/backflush mode, the desorption vent is closed and the capillary trap is flash heated to a temperature in the range of ambient to $300\text{ }^{\circ}\text{C}$ ($13\text{ }^{\circ}\text{C}/\text{sec}$) injecting the compounds on the capillary column. The capillary trap, desorption vent, and capillary column are connected using a hexagonal nut, a low volume T-piece. To remove any remaining compounds the adsorption trap is heated for a short period to a temperature higher than the one in the sample transfer mode and again using a reversed carrier gas flow. Before sampling is restarted, the adsorption trap is cooled to the desired temperature. Analysis time is optimized to allow separation of the components of interest, cool down to, and equilibration at the initial temperature setting before the sampling period is over.

The consumption of liquid nitrogen for cooling purposes is reduced by minimizing the mass of the traps and maximizing the efficiency of the cooling process. For typical conditions (temperatures of the adsorption trap at $-50\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$, of the capillary trap at $-100\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$, a cycle time of 1 hr), the consumption approximates 1.5 L/hr. Commercially available liquid nitrogen containers of 1000 L allow unattended operation for nearly four weeks. An alternative system is a vortex cooling for the adsorption trap and a liquid nitrogen generator for the capillary trap. The power consumption of this alternative system is high but refill of the liquid nitrogen container is required infrequently. Detector gases, hydrogen and air, can be generated at the site or supplied in cylinders, sufficient for four weeks. The carrier gas, helium, is also supplied in cylinders.

Calibration is performed by replacing the sample stream by a stream of clean air containing compounds released from cylinders (for the very volatile compounds, like ethane, propene, and butane) and a set of permeation tubes (for the volatile compounds like hexane, benzene, and dichloroethane).

Data processing is carried out in three stages. After integration of the detector signals, the peaks are identified using relative retention times. These retention times are corrected for shifts caused by random variations and drifts in the analytical conditions. This correction is partly directed by prior knowledge of the occurrence of individual reference compounds as well as of the pattern. Using this method, the accuracy of identification is maximized and any malfunction of the system will be indicated by missing reference peaks. Furthermore, the responses of the two detectors are compared to improve the quality of identification and quantitation. The results and the indication for the quality of the data processing may then be transmitted to the central computer systems using standard communication software and hardware.

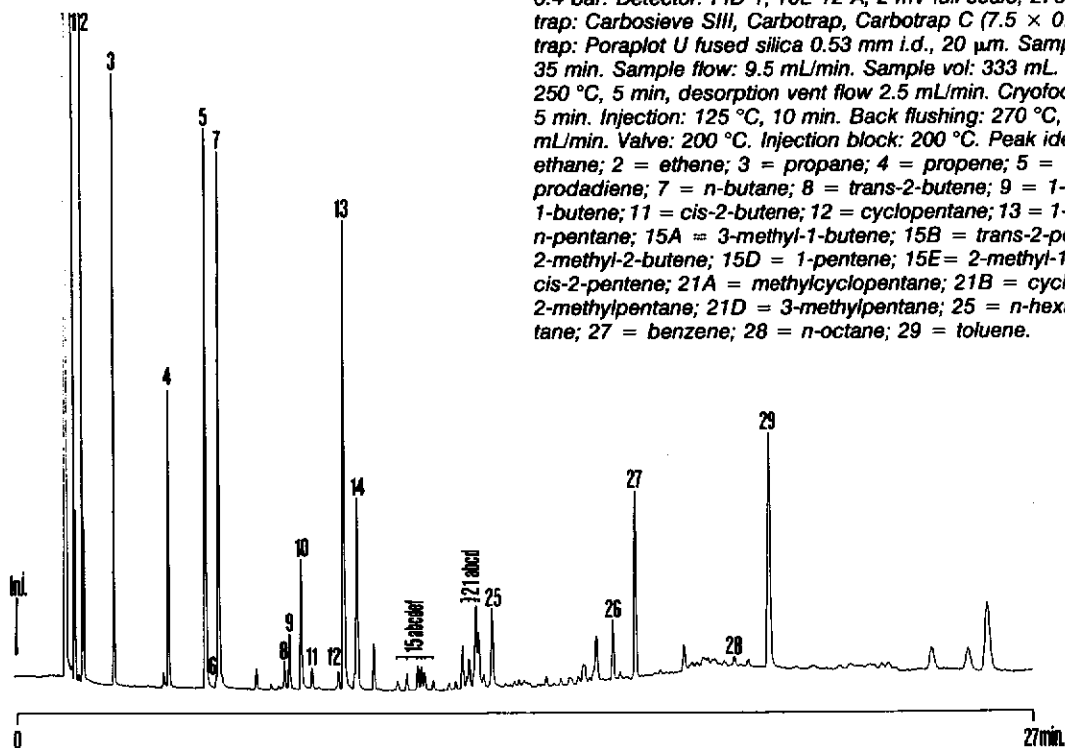


Figure 3 Chromatogram of an air sample. Sample: Outdoor air at Bilthoven Station, June 22, 1990, at 15.00 hr. Column: fused silica 25 m \times 0.53 mm i.d. $\text{Al}_2\text{O}_3/\text{KCl}$, $df = 10 \mu\text{m}$. Temperature: 40 $^\circ\text{C}$, isothermal 1 min, programmed to 200 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$, 200 $^\circ\text{C}$, isothermal 30 min. Carrier: He 0.4 bar. Detector: FID 1, $10\text{E}-12 \text{ A}$, 2 mV full scale, 275 $^\circ\text{C}$. Adsorption trap: Carbosieve SIII, Carbotrap, Carbotrap C (7.5 \times 0.29 cm). Capillary trap: Poraplot U fused silica 0.53 mm i.d., 20 μm . Sample coll.: -20 $^\circ\text{C}$, 35 min. Sample flow: 9.5 mL/min. Sample vol: 333 mL. Sample desor.: 250 $^\circ\text{C}$, 5 min, desorption vent flow 2.5 mL/min. Cryofocusing: -150 $^\circ\text{C}$, 5 min. Injection: 125 $^\circ\text{C}$, 10 min. Back flushing: 270 $^\circ\text{C}$, 10 min, flow: 20 mL/min. Valve: 200 $^\circ\text{C}$. Injection block: 200 $^\circ\text{C}$. Peak identification: 1 = ethane; 2 = ethene; 3 = propane; 4 = propene; 5 = 1-butane; 6 = prodadiene; 7 = n-butane; 8 = trans-2-butene; 9 = 1-butene; 10 = 1-butene; 11 = cis-2-butene; 12 = cyclopentane; 13 = 1-pentane; 14 = n-pentane; 15A = 3-methyl-1-butene; 15B = trans-2-pentene; 15C = 2-methyl-2-butene; 15D = 1-pentene; 15E = 2-methyl-1-butene; 15F = cis-2-pentene; 21A = methylcyclopentane; 21B = cyclohexane; 21C = 2-methylpentane; 21D = 3-methylpentane; 25 = n-hexane; 26 = n-heptane; 27 = benzene; 28 = n-octane; 29 = toluene.

Application

The above-described analyzer is used by the Dutch National Air Quality Monitoring Network (NAQMN). The variables include: the nature of the trapping material, the capillary column, temperatures of the traps, time of the different modes, and flows of the sample stream and desorption vent. The characteristics of the compounds of interest guide the selection of these variables. Monitoring compounds in relation to the biospheric ozone formation, such as aliphatic and olefinic hydrocarbons as well as the alkyl aromatics, requires a chromatographic column with a high resolution of the very volatile organic compounds, such as ethene and ethane. For this purpose, the $\text{Al}_2\text{O}_3/\text{KCl}$ PLOT column is selected. The NAQMN VOCAA has a cycle time of 1 hr. The conditions of this monitor are given in Figure 3 along with a chromatogram of a sample taken on a day with normal levels of air pollutants.

Other applications, such as the monitoring of CFC (chlorofluorocarbons), require a different configuration of column and trapping material. The $\text{Al}_2\text{O}_3/\text{KCl}$ column is not suitable for these compounds, since partly halogenated compounds decompose at high temperatures.⁵ A thick film WCOT column or a porous polymer PLOT column should be used in this case.

Conclusion

The most significant characteristic of the VOCAA is

the simultaneous sampling and analysis of (very) volatile organic compounds at a frequency of 1 hr or less. During a maximum of 25% of the time, no sample is taken, which is acceptable. This time is utilized by the sample transfer and the backflush mode. Using thick film WCOT or porous PLOT columns, the compounds that can be monitored range from the unsaturated and saturated alkanes, benzene, and the substituted aromatics and various halogenated compounds. The high resolution power of capillary columns allows high quality identification and quantitation and produces information concerning individual compounds relevant in atmospheric processes.

References

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